Continental J. Environmental Sciences 9 (2): 22 – 36, 2015 ISSN: 2141 - 4048
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Printed in Nigeria doi: 10. 5707/cjenvsci.2015.9.2.22.36

RESEARCH PAPER

DETERMINATION OF PHYSICO-CHEMICAL PROPERTIES AND METAL CONCENTRATIONS OF HAND DUG WELLS AROUND A DUMPSITE IN AKURE, ONDO STATE, NIGERIA

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ABSTRACT

The physiochemical properties and heavy metal concentration of groundwater from various locations in Maronu street, Akure metropolis were analysed using standard methods of analysis. The sample taken from nine different locations within the vicinity of a dumpsite revealed: physico-chemical parameter: Temp (27.70 – 29.60^{0}C), pH 9.2 – 9.4, TDS (130 – 244 mg/L), Total hardness (59 – 190 mg/$CaCO_3$), Cl^- (32 – 265 mg/L), SO_4 (10.50 mg/L) and PO_4 (1.50 – 3.10 mg/L). The ranges of metal concentrations were: Na (10.80 – 25.70mg/L), Ca (27 – 124mg/L), K (12.50 – 19.10mg/L), Mg (0.94 – 3.25mg/L), Fe (0.75 – 1.22mg/L), while the values for Pb, Ni, Zn and Cu were low. The parameters determined in the water samples were within the World Health Organisation (WHO) and Standard Organisation of Nigeria (SON) permissible limits. The conclusion from the study indicated that the water samples are safe for consumption, but it is highly recommended that constant monitoring should be ensured in other to avoid intake of polluted water.

KEYWORDS: Pollution, ground water, drinking water, waste dump, WHO, SON.

Received for Publication: 11/08/15 Accepted for Publication: 05/11/15
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INTRODUCTION

Water is a universal drink that is generally accepted by living things. It has got many uses depending on the user. The various sources of water include: underground, surface and rain. Water as a universal solvent has the ability to dissolve many substances, but it is almost impossible to have water in its pure form, since it cannot be held up in a vacuum.

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Generally, hand dug wells are one of the main sources of water used in Akure, Nigeria. Uncensored human activities in development countries contribute immensely to the poor quality of groundwater. Acute problems are often encountered in areas which are densely population, with localization of industries. Water for human consumption must be free from organisms and chemical substance in concentration large enough to affect health (Hogain *et al*., 2011). Addition of various pollutants through sewage, industrial effluent, agricultural run-off, dumpsite and so on into the water main stream bring about a series of changes in the physico-chemical characteristics of the water, which have been the subject of different investigations (Yeboah *et al*., 2013; Waziri *et al*., 2012).

The public health significance of water quality cannot be over emphasized. Many infections disease are transmitted by water. According to World Health Organisation (WHO), about 5 million children are killed annually and make $1/6^{th}$ of the world population sick (WHO, 2004). In Nigeria, majority of the rural populace do not have access to potable water and therefore, depends on well, stream and river water for domestic use.

The bacteria qualities of groundwater, pipe borne water and other natural water supplies in Nigeria, have been reported to be unsatisfactory, with coliform counts exceeding the level recommendation by WHO (2011).

The reason for elucidation of important parameters in water quality assessment may be attributed to the fact that in the overall portability of water, such parameters should not be ignored (Osuinde and Enuezic 1999).

Waste dump site is one of the contributing factors to environmental hazards. They have been useful indicators to atmospheric and water pollution. In view of the evidence of the adverse effects of dumpsites on water consumption, not much data from this part of Akure city, Nigeria have been published or in existence. Analysis of water samples from this area would not be a waste as it would contribute to existing knowledge on water pollution and assist on further plans with regards to water consumption.

The objective of this study was to determine the physico-chemical parameters and heavy metals concentrations of waters from hand dug wells located around dumpsite in Akure, Nigeria.

MATERIALS AND METHODS

Sample Collection

Water samples were collected from nine different well in Maronu Street around new stadium Araromi of Akure Metropolis, Nigeria. The plastic containers used for the collection of the sample were washed with detergent. The containers were rinsed twice with the water sample

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before the samples were taken. The samples were transferred to the laboratory for physical, chemical and heavy metal determinations.

Physicochemical Analysis
The water samples collected were analyzed for pH, temperature, colour, turbidity, conductivity, total dissolved solids, suspended solid, total solid, acidity, alkalinity, total hardness, chloride, nitrate, sulphate and phosphate.

Alkalinity
All the glass wares used were washed and rinsed with distilled water. 0.02N of H_2SO_4 was poured into a burette. 100ml of water sample was measured to the conical flask and 3 drops of phenolphthalein was added and vigorously shaken. It was then titrated against the 0.02N of sulphuric acid (H_2SO_4) and continuously shaken until the colour changed from a colourless to pink.

Total hardness
All the glass wares used were washed and rinsed with distilled water. 100ml of the water sample was measured into a conical flask, and 5ml of buffer solution was added and 1 spatula of Eriochrome Black T was also added to it, EDTA was poured into burette and it was titrated against the waters sample and was shaken vigorously until the colour changes from pink to blue.

pH
One hundred militer (100ml) of water sample was measured into a beaker. A calibrated pH meter was cleansed with cotton wool containing distilled water and the electrode was dipped into the measured 100ml of water sample and the reading was taken on the meter.

Chloride
All glass wares used were washed and rinsed with distilled water. 0.01N of Silver Nitrate was poured into the burette to the mark. 100ml of Potassium Chromate ($K_2Cr_2O_7$) was added into the water sample and was titrated against the 0.01N Silver Nitrate ($AgNO_3$) and was continually shaken until the colour changes from yellow to reddish brown.

Total Dissolve Solid
One hundred militer (100ml) was measured into a beaker. A calibrated TDS meter was cleaned with cotton wool containing distilled water and the electrode was dipped into the measured water sample and the reading was taken.

Acidity
Fifty militer (50ml) of the sample was pipetted into a 250ml beaker, the pH of the sample was measured, 5ml increments of standard of H_2SO_4 was added to lower the pH to 4.0, 5 drop of

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H_2SO_4 was added, the sample was heated to boiled for 2 to 4 minutes. After heating the sample was discoloured and allowed to cool at the room temperature, it was then titrated with standard NaOH solution to pH 8.2. Phenolphthalein was used as an indicator and the colour change while hot from colourless and to pink.

Total Suspended Solid and Total Solid (TSS and TS)
The initial weight of the crucible was weighed 20ml of fitter water sample was measured into it, the crucible was placed inside the oven at 103^0C after drying in the oven, it was cool to room temperature inside the desiccator. The final dry weigh of the crucible was noted.

Phosphate
Twenty militer (20ml) of the sample was acidified with concentrated Nitric acid to which a little Ammonium Molybdate was added. The presence of phosphate ion was indicated by the formation of a bright yellow precipitate layer.

Turbidity
A two part calibrated turbidity tube was used with calibrations from 5-25 turbidity units. The joined tubes were held over a white paper, while slowly pouring the water sample into the tube until the black cross at the bottom was no longer visible. At this point the reading was taken from the side of the tubes as the turbidity value of the water sample.

Temperature
The temperature of the water samples were measured using mercury in glass thermometer on site *(in-situ)*.

Conductivity
The conductivity of the sample was measured using conductivity meter.

Colour Measured
A 20ml volume of each water sample was poured into a clean beaker. The sample was then shaken vigorously to check for any frothing and allowed to settle. Then the colour was determined

Nitrate
Test tube was filled with sample to 20ml and one level spoonful of nitratest power containing Zinc dust and Barium Sulphate and one nitratest tablet (Ammonium Chloride) were added and was shaken for a minute. The tube was allowed to stand for a minute and was inverted 3-4 times to aid flocculation and allowed to stand for two minutes to ensure complete settlement. The cleared solution was dispersed into tube to 10ml mark and one nitricol tablet (sulfanilic acid, acting as the aromatic amine); was added, crushed and mixed to dissolved, then it was allowed to

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stand for ten minutes for colour development and readings were taken on the photometer at 570mm wavelength.

Sulphate

Between 100 to 400ml of the water was taken and was filtered, 1:1HCL was added in drops until acid to litmus, three drops was added in excess and was evaporated to 50ml, the solution was boiled and boiling barium chloride solution was added until all the sulphate precipitate. It was digested on a water bath until the precipitate has settled. A sintered-glass crucible was dried to constant weight. It was then connected to the filtering equipment and the vacuum pump and the precipitate was filtered through sintered-glass crucible.

It was washed for a number of times with hot water until the filtrate was chloride free ($AgNO_3$ Test) crucible precipitate was dried in an oven at 103-150^{0}C constant weigh.

HEAVY METAL ANALYSIS

Atomic Absorption Spectrophotometer (AAS) Bulk Scientific Model 210VGS was used for the measurement. Five milliliter (5ml) of water sample was added in reaction cell, 5 drops of the metal reagent was then added and mixed. The concentration of the following metal (lead, zinc, iron, magnesium, sodium, calcium, potassium cadmium, nickel and copper) was determined in the AAS (Stewart, 1989).

Statistical Analysis

The results obtained in this research work were subjected to statistical analysis: Maximum, Median, Mode, Mean, Standard Error Mean, Standard Deviation, Minimum, Coefficient of variation, correlation coefficient, histogram and others using Minitab 16 Statistical Software.

RESULTS AND DISCUSSION

Figure 1 and Table 1 depict the results and statistical calculations of the physico-chemical parameters of the well water samples analysed.

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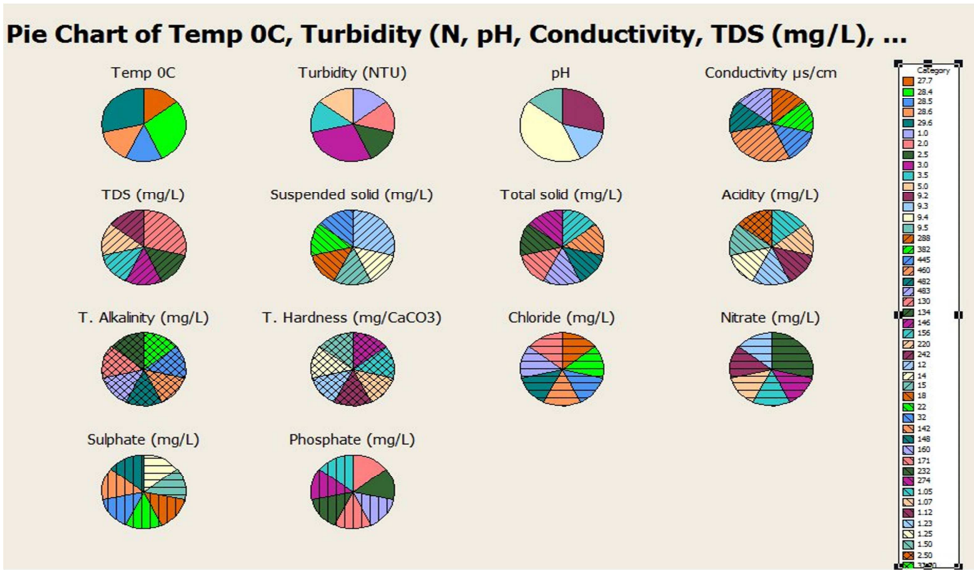

Fig 1. The results of physico-chemical properties of samples

Table 1. Statistical results of the variables determined

Variable	Total Count	N	N*	Maximum	Mean	SE Mean	StDev	Min
Temp 0C	7	7	0	29.600	28.686	0.260	0.689	27.7
Turbidity (NTU)	7	7	0	5.000	2.857	0.472	1.249	1.0
pH	7	7	0	9.500	9.3429	0.0429	0.113	9.2
Conductivity µs/cm	7	7	0	483.0	428.6	26.7	70.7	288.0
TDS (mg/L)	7	7	0	242.0	165.4	17.5	46.2	130.0
Suspended solid (mg/L)	7	7	0	32.00	17.86	2.71	7.17	12.00
Total solid (mg/L)	7	7	0	274.0	183.3	18.9	50.0	142.0
Acidity (mg/L)	7	7	0	2.500	1.389	0.194	0.513	1.050
T. Alkalinity (mg/L)	7	7	0	75.35	59.11	4.97	13.14	32.50
T. Hardness (mg/CaCO3)	7	7	0	190.0	115.7	16.9	44.8	59.0
Chloride (mg/L)	7	7	0	265.0	146.4	25.6	67.9	32.0
Nitrate (mg/L)	7	7	0	22.25	13.31	1.56	4.12	10.50
Sulphate (mg/L)	7	7	0	69.00	46.79	5.34	14.14	32.00
Phosphate (mg/L)	7	7	0	3.100	2.186	0.196	0.518	1.500

Variable	Variance	CoefVar	Sum	Sum of Squares	Minimum	Q1
Temp 0C	0.475	2.40	200.800	5762.940	27.700	28.400
Turbidity (NTU)	1.560	43.71	20.000	66.500	1.000	2.000
pH	0.0129	1.21	65.4000	611.1000	9.2000	9.2000
Conductivity µs/cm	4998.6	16.50	3000.0	1315706.0	288.0	382.0
TDS (mg/L)	2134.3	27.93	1158.0	204372.0	130.0	130.0
Suspended solid (mg/L)	51.48	40.18	125.00	2541.00	12.00	12.00

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Total solid (mg/L)	2498.2	27.27	1283.0	250145.0	142.0	148.0
Acidity (mg/L)	0.263	36.96	9.720	15.077	1.050	1.070
T. Alkalinity (mg/L)	172.60	22.22	413.80	25497.07	32.50	58.00
T. Hardness (mg/CaCO3)	2007.6	38.72	810.0	105774.0	59.0	64.0
Chloride (mg/L)	4604.4	46.36	1024.5	177569.3	32.0	128.0
Nitrate (mg/L)	16.94	30.92	93.19	1342.28	10.50	10.50
Sulphate (mg/L)	199.95	30.22	327.51	16522.93	32.00	32.91
Phosphate (mg/L)	0.268	23.69	15.300	35.050	1.500	1.800

Variable	Median	Q3	Maximum	Range
Temp 0C	28.500	29.600	29.600	1.900
Turbidity (NTU)	3.000	3.500	5.000	4.000
pH	9.4000	9.4000	9.5000	0.3000
Conductivity µs/cm	460.0	482.0	483.0	195.0
TDS (mg/L)	146.0	220.0	242.0	112.0
Suspended solid (mg/L)	15.00	22.00	32.00	20.00
Total solid (mg/L)	160.0	232.0	274.0	132.0
Acidity (mg/L)	1.230	1.500	2.500	1.450
T. Alkalinity (mg/L)	59.50	65.50	75.35	42.85
T. Hardness (mg/CaCO3)	125.0	136.0	190.0	131.0
Chloride (mg/L)	148.0	156.0	265.0	233.0
Nitrate (mg/L)	12.04	14.01	22.25	11.75
Sulphate (mg/L)	42.50	59.00	69.00	37.00
Phosphate (mg/L)	2.100	2.500	3.100	1.600

Temperature

The results of the water samples with regard to temperature ranged between 27.7 and 29.6^{o}C with a mean of 28.69 and standard deviation of 0.7 (Fig 1). All the samples have high temperatures. This is expected because the samples are located in a temperate region. Our results are similar to 28.3 – 28.85^{o}C provided by Olomukoro and Oviojie (2014), but somehow lower to 30^{o}C recorded for water samples from India (Roy, 2007). The results of our study are within the WHO limits of 5 - 50^{o}C.

Turbidity

The mean result is 2.86, while the standard error is 0.47. The range data of the study (1.0 – 5.0) were lower than 3.58 – 8.17 (Olomukoro and Oviojie, 2014), 1.71 – 7.42 (Waziri *et al*., 2012) and 9. 27 (Olowoyo, 2011). It was observed too that the results obtained from this study were higher that the results (0.0 – 0.6) of Olaoye and Olaniyan, (2012). In all the results were within WHO limit of 5. Turbidity is an expression of optical property wherein light is scattered by suspended particles in water. Turbidity affects light scattering, absorption properties and aesthetic appearance in a water body.

Electrical Conductivity

The results (Fig 1) were within 288 - 483µs/cm with coefficient of variation of 16.50% this means the results were not highly varied. The results compared with the results obtained from rain water samples from India (Subramani and Devaanandan, 2015). Electrical conductivity is the numerical expression of the water's ability to conduct an electrical current. The conductance of the samples gives rapid and practical estimate of the variation in dissolved mineral content of

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water supply (Wetzel, 2001). This parameter is a factor for the determination of water purity that depends on the nature and concentration of ionized substances in the water at water temperature (Chughtai *et al*., 2014).

Total Dissolved Solids

Total Dissolved Solids (TDS) of the water samples ranged from 130 to 242mg/L (Fig 1). They compared with the results in rainwater samples from Maiduguri, Nigeria (Waziri *et al*., 2012) and Karachi, Pakistan (Chughtai *et al*., 2014). The TDS values were higher than 19. 37 – 33.38mg/L obtained by Olowoyo, 2011. The results obtained fell within 0 to 2900mg/L of UNESCO standard. According to Hamhill and Bell (1986) the water samples from this region will be suitable for livestock. According to Wetzel (2001) TDS are solids that are in dissolved state in solution. Presence of high TDS will give the water inferior palatability. Also may induce an unfavourable physiological reaction in the consumer.

Total Suspended Solid (TSS)

The values of TSS ranged from 12.00 to 32.00mg/L with standard error mean of 2.71. The lowest were obtained from the control (SWC) and SW4 while, the highest was obtained in SW1. The values were higher than results obtained by Olowoyo (2011) and 5mg/l standard set by WHO. TSS this is part of solids retained on filter of standard specific size (generally 2.0µ) under specific conditions. High TSS is not good for bathing, industrial and other uses.

Acidity

Our analysis results produced 1.05 and 2.50mg/L with a variance of 0.263. The results are far less than the results of Subramani and Devaanandan (2015) from rain water. The difference might be due to the industrial activities of the environment. According to De (2003) acidity contribution is mainly due to dissolution of gases such as CO_2, SO_x and NO_x. In water analysis, acidity test does not bear significant importance because methyl orange acidity invariably remains absent in the raw water and even phenolphthalein acidity normally does not exist to a significant extent in the raw water (Kumar, 2014).

Alkalinity

The results obtained for alkalinity were 32.50 - 75.35mg/L, mean 59.11 and standard error 4.97. These results compared with rain water from Pondicherry, India (Subramani and Devaanandan, 2015) and Lagos, Nigeria (Dinrifo *et al*., 2010). Alkalinity is the measure of the capacity of water to buffer acids or acid neutralizing capacity. Alkalinity has many applications and treatment of natural waters and wastewaters. Alkalinity measurements are used in determining the suitability of water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than or only slightly greater than that of the water supply.

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Total Hardness

T. Hardness values in mg/$CaCO_3$ were between 59.0 and 190.0 with a standard deviation. The lowest is found in SW2 and the highest is obtained in SW1. Based on the coefficient of variation, the results within the samples were not highly varied. The results in this work are within WHO (1999) permissible limits of 100 – 500mg/L. However, the results were higher than the hardness recorded for rainwater samples in Nigeria (Olowoyo, 2011), India (Subramani and Devaanandan, 2015) and Pakistan (Chughtai *et al*., 2014). Hardness is predominantly caused by divalent cations such as calcium, magnesium, alkaline earth metal such as iron, manganese, strontium, etc. Temporary hardness is caused by carbonates and bicarbonates of calcium and magnesium, while permanent hardness is caused by sulphates and chlorides (Wetzel, 2001). Harness chart for drinking water has: Soft (0 – 60mg/L), Medium (60 - 120mg/L), Hard (120 – 180mg/L) and Very hard (> 180mgl). In line with this chart, the water samples are within medium and hard categories.

Chloride

This parameter ranged between 32.00 and 265.0mg/L. The chloride is in agreement with results obtained by Adeyeye and Abulude (2004), but significantly higher in content when compared with results (16.37 – 58.27mg/L) of hand dug wells in Udu Community in Niger Delta region, Nigeria. Both Udu and our results were within the WHO (2011) and Standard Organization of Nigeria (SON) permissible limits (250mg/L). In natural waters, the presence chlorides are attributed to the dissolution of salt deposits in the form of ions (Cl^-). High chloride contents may indicate pollution by sewage, industrial wastes, intrusion of seawater or other saline water. High Cl^- contents has a deleterious effect on metallic pipes and structures and agricultural plants. The high values obtained in this paper could be due to the waste dumpsites in the vicinity.

Nitrate

The results obtained for this is as follows: Range: 10. 50 - 22.25mg/L, Mean: 13.31, Std Error: 1.56, Std Dev.: 4.12 and Coefficient of variation: 30.92%. Nitrates are the most oxidized forms of nitrogen and the end product of the aerobic decomposition of organic nitrogenous matter. Sources of nitrates are chemical fertilizers from cultivated lands, drainage from livestock feeds, domestic and industrial sources. According to Wetzel, (2001) the main source of polluting nitrates is domestic sewage.

Sulphate

The lowest sulphate value in the study was 32.00mg/L found in control (SW1) while the highest 69.00mg/L (SW3). In comparison with other research works, these results were higher than he results of hand dug wells (Olomukoro and Oviojie 2014) and water samples from Block Phunda (Bhopal), India (Roy, 2007), whereas the present results were comparable to those of Subramani and Devaanandan (2015) and Chughtai *et al*. (2014). Sulphates are found appreciably in all natural waters, particularly those with high salt content. Also, industrial pollution and domestic

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sewage, biological oxidation of reduced sulphur species add to sulphate content. When soluble in water, it impacts hardness with other cations. Sulphate causes scaling in industrial water supplies, and odour and corrosion problems due to its reduction to hydrogen sulphide (Wetzel, 2001).

Phosphate

The phosphate content in the water samples are presented in Fig 1. The presence of phosphate in water is due to detergents, used boiler water, fertilizers and biological processes. They occur in natural or waste waters as orthophosphates, condensed phosphates and naturally found phosphates.

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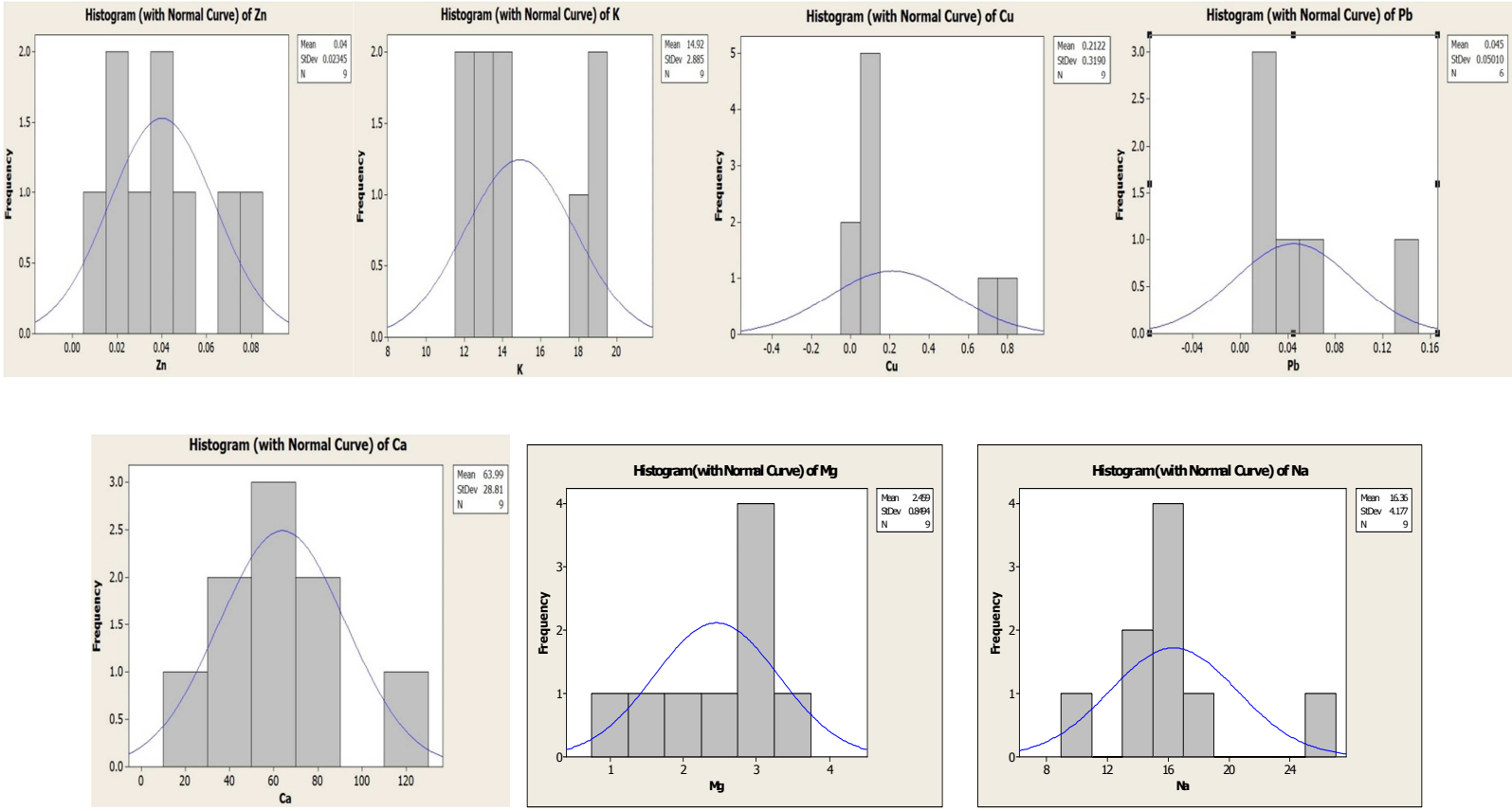

Fig 2: The normal curves of the metals (Zn, K, Cu, Pb, Ca, Mg and Na) in the water samples

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Fig 2 depicts the normal curves of the metals (Zn, K, Cu, Pb, Ca, Mg and Na) in the water samples. The analysis of calcium revealed a range of 72.6, 72.70, 124.00 65.00, 41.8, 33.50, 69.00 and 67.30 mg/L respectively. Samples SW6 and SW7 were below the WHO standard of 100-300mg/L while others were within the range. Magnesium concentrations in the samples were in the range of 3.25, 3.10, 2.94, 1.25, 2.50, 2.99, 3.14 and 2.15 mg/L. These results were within the tolerated limit (20mg/l) both (calcium and Magnesium) cations are the major cause of hardness in water (WHO, 2010). Iron concentrations were above 0.3mg/L approved by WHO. It is noted that anaerobic groundwater may contain ferrous at concentration of up to several mg/l without discoloration or turbidity in water when directly pumped from well (SON, 2007; WHO, 2010). Results for Na were below the permissible standard (200mg/L). Sodium can occur naturally or as a result of road salt application, water treatment. Sodium is not considered to be toxic. The human body needs sodium in order to maintain blood pressure, control fluid levels and for normal nerve and muscle function (WHO, 2010). Cadmium was not detected in most of the sample except for SW8 which was 0.01mg/L and above the tolerated limit of WHO (0.003mg/L). The Cu values in the samples were 0.06, 0.05, 0.03, 0.04, 0.01, 0.7 0.06, 0.09 and 0.07 mg/L respectively. The concentrations were far less than the WHO permissible limit only sample SW6 was within the standard (1.0mg/L). Pb contents in the sample were within the tolerated limits. But lead was not detectable in samples SW3, SW8 and SWC. It should be noted that exposure to lead through water is generally low in comparison with exposure through air, or food to some extent, but analysis of both surface and groundwater suggest that lead concentration is fairly low. K concentrations in the sample were above the permissible limit (10.0mg/L). Ni in the sample was not detectable, except SW4 which was 0.01mg/L. Nickel is released into the environment by power plant, metal factories and waste incinerator. It is also used in fertilizer and enters groundwater from farm runoff. Nickel is necessary in human diet but can become carcinogenic and toxic in high doses (WHO, 2005).

Table 2: Correlation constants of Metals

	Na	Ca	K	Pb	Zn	Mg	Cu
Ca	0.783	1					
K	0.053	0.599	1				
Pb	0.742	0.921	0.999	1			
Zn	0.092	0.725	0.690	0.213	1		
Mg	0.448	0.080	0.510	0.396	0.045	1	
Cu	0.601	0.229	0.633	0.654	0.831	0.164	1
Fe	0.656	0.749	0.775	0.062	0.033	0.050	0.515

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The correlation constants in Table 2 indicated that these pairs Pb/Ca (0.921) and Pb/K (0.999) had strong correlations while Ca/Na, Pb/Na, Zn/Ca, Cu/Zn, Fe/Ca and Fe/K possessed moderate correlations. According to Mehta (2011), correlation constants are statistical tools that are useful to find predictable relationships which can be exploited in practice. Also they are used for the measurement of the strength and statistical significance of the relation between two or more water quality parameters. Hence, are helpful tools for the promotion of research activities (Joshi *et al*., 2009).

CONCLUSION

The concentrations of physico-chemical and heavy metals have been considered in this paper. Standard and statistical methods of analyses have been used for the assessments. The results obtained have been compared with WHO, SON standards and other research works on water samples. It was noted that the control (distilled water) compared favourably with the well samples. On a final note, it can be concluded that despite the location of wells near a waste dump site, the water samples are good for consumption and industrial purposes, but regular monitoring must be put in place to avoid intake or use of polluted water.

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